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THE THERMAL DECOMPOSITION OF ORGANIC NITRATES III:
THE AFFECT OF ADDITIVES ON THE THERMAL DECOMPOSITION
OF ETHYL NITRATE

19 AUGUST 1953

U. S. NAVAL ORDNANCE LABORATORY

WHITE OAK, MARYLAND

THE THERMAL DECOMPOSITION OF ORGANIC NITRATES III.
THE AFFECT OF ADDITIVES ON THE THERMAL DECOMPOSITION
OF ETHYL NITRATE

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ABSTRACT: The optical techniques developed earlier for the
study of the vapor phase thermal decomposition of nitrate
esters have been applied to the study of the effects of
various additives on the thermal decomposition of ethyl
nitrate.

The results of these studies have been interpreted in terms
of a revised mechanism proposed in preliminary form in an
earlier report and in completed form here. These results give
strong support to the revised mechanism.

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The research reported herein was carried out under Task
Assignment NOL-Re2d-02-1-52,53. The optical techniques
previously developed have been applied to further studies
on the thermal decomposition of ethyl nitrate. Data has
been obtained which help to support and complete the
mechanism previously developed for the thermal decomposition
of nitrate esters.

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                              By direction

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ILLUSTRATIONS

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INTRODUCTION

The organic nitrates constitute a class of compounds very important in the field of propellants. Thus nitroglycerine and nitrocellulose are outstanding examples of this group. In an effort to gain information about the way in which these compounds ignite and burn many workers have studied the thermal decomposition of many simple nitrate esters chiefly from the kinetic point of view (a, b, c, d, e).

This report is the third (f, g) in a series describing the application to this problem of the infrared spectrometer as an analytical tool. In preceding reports the development of the analytical technique and its application to the study of the thermal decomposition of ethyl nitrate (b) and n-propyl and t-butyl nitrates (g) have been described. The results observed have raised many questions about the mechanism of nitrate ester decomposition which previously accepted ideas could not answer. It had been possible to develop a revised mechanism (g) which is capable of explaining most of the results observed in this laboratory and by the other workers in the field.

The work described in this report is concerned with further studies of ethyl nitrate. Chiefly it deals with the effect of various additives on the thermal decomposition of ethyl nitrate. It is felt that with the experimental results reported here it is possible to give a fairly complete picture of the reaction and an attempt is made here to do so.

EXPERIMENTAL PART

Apparatus and Chemicals. The infrared analyses of the gas mixtures were made with a Perkin-Elmer Model 12-C Infrared Spectrometer equipped with a rock salt prism. The measurements of nitrogen dioxide were made on a Beckman Model DU Quartz Spectrophotometer. The infrared spectra shown in the illustrations were taken on a Perkin-Elmer Model 21 Double Beam Spectrometer equipped with a rock salt prism.

Ethyl nitrate was Eastman Kodak White Label Grade which was redistilled. A fraction boiling at $87.5 - 87.8°C$ was used.

Acetaldehyde was Eastman Kodak White Label Grade. It was used directly from the bottle.

The nitrogen dioxide was purchased from the Matheson Company and was rated as better than 95% pure, the impurities being the other oxides of nitrogen. It was distilled unto the vacuum system through a tube of anhydrous calcium sulfate.

The nitric oxide used was purchased from the Matheson Company and was rated as 99% pure. When admitting nitric oxide to a bulb on the vacuum system from the tube where it had been condensed with liquid nitrogen, it was standard practice to allow the nitric oxide to warm up only enough to give the desired pressure. Due to the high relative volatility of nitric oxide this effected a further purification. It was possible to show that this gave nitric oxide entirely free of any nitrogen dioxide, for example.

The oxygen used was taken directly from an oxygen cylinder.

The diethyl peroxide was prepared as described by Harris and Egerton (h). The final distillation at atmospheric pressure yielded a product boiling at $62.5 - 63.5^{\circ}C$. It was stored in sealed ampules in a refrigerator.

The nitromethane was Eastman White Label Grade and was used directly from the bottle. The formaldehyde used was generated by heating a tube containing paraformaldehyde. In the time interval between filling the bulb with formaldehyde and putting it in the bath, no depositing of the formaldehyde in the form of its polymer on the sides of the bulb could be seen.

The Experimental Techniques. The methods of making the measurements and manipulating the gas mixtures have been described in a previous report (f). The experiments with oxygen and the analyses for nitromethane involved slightly different techniques however and so are described here.

The Experiments with Oxygen. In the experiments with oxygen it was not possible to condense the oxygen completely into the reaction bulb. Knowing the pressure in the measuring bulb and observing the residual pressure after the bulk of the oxygen had been transferred, it was possible to calculate how much was in the reaction bulb.

The Nitromethane Experiments. The nitromethane was separated from the ethyl nitrite in the decomposition mixture by the use of traps. After the reaction bulbs had been broken in the break-off apparatus in the usual way, the gases were pumped first through a trap at -50 to $-60^{\circ}C$ and then through one at liquid nitrogen

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temperature. Examination of the spectra of the two fractions at the nitromethane doublet, 6.25-6.40μ, showed quite clearly that little, if any, nitromethane passed the first trap. To analyze for the nitromethane the 6.25-6.30μ peak of the doublet was used. For this analysis the double beam spectra were used. Spectra at three pressures were taken for the Beer's law constant.

Table 1

The Absorption of Nitromethane

at 6.30μ   (cell length = 52mm)

P (mm)	Log Io/I(D)	D/p
5.0	0.256	0.051
7.0	0.370	0.054
9.2	0.506	0.053

The value D/p = 0.053 was used. This is certainly good to about 10% and this was sufficient for the purpose.

RESULTS AND DISCUSSION

In preceding reports (g,1) the following mechanism has been discussed:

$$C_2H_5ONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_5O. + NO_2 \qquad (1)$$

$$C_2H_5O. + NO \overset{k_2}{\longrightarrow} C_2H_5ONO \qquad (2)$$

$$C_2H_5O. \longrightarrow CH_3. + CH_2O \qquad (3)$$

$$CH_3. + NO_2 \longrightarrow CH_3NO_2 \qquad (4)$$

$$NO_2 + CH_2O \longrightarrow NO + CO + CO_2 + H_2O \qquad (5)$$
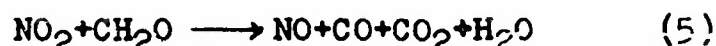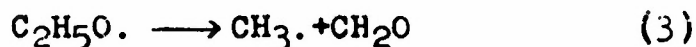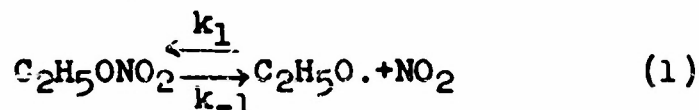
This mechanism has been, in a sense, incomplete since it did not appear that sufficient nitric oxide could arise via (5) to give the ethyl nitrite yields observed. For reasons that will be discussed later in this report the following step

seems capable of completing the picture

$$2CH_3 \cdot + 7NO_2 \longrightarrow 2CO_2 + 3H_2O + 7NO \qquad (6)$$
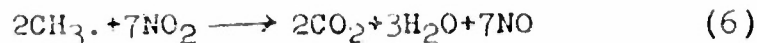
If the above scheme is treated kinetically making the steady state assumption for ethoxyl radical, the following expression results:

$$\frac{-d\ln(C_2H_5ONO_2)}{dt} = \frac{k_1}{1 + \dfrac{k_{-1}(NO_2)}{k_2(NO) + k_3}} \qquad (7)$$

It is interesting and informative to consider the various aspects of this problem from the point of view of the above mechanism and rate expression. This will be done first for the studies involving the additives.

The Effect of Additives on the Thermal Decomposition of Ethyl Nitrate.

Nitrogen Dioxide. L. Phillips (e) reported that nitrogen dioxide in amounts comparable to the ethyl nitrate present lowers the rate of thermal decomposition markedly. His results have been confirmed by Pollard, Wyatt and Marshall (j). The latter group reported that addition of larger amounts of nitrogen dioxide accelerated the reaction. Both of these studies involved the use of manometric techniques.

The results of a number of experiments on the effect of nitrogen dioxide are shown in Table 2.

Table 2

The Effect of Nitrogen Dioxide on

the Rate of Decomposition of Ethyl Nitrate at 181°C

Exp.	Initial Pressure [a] (mm)		t (min.)	Percent Reaction
	Ethyl Nitrate	Nitrogen Dioxide [b]		
1	22.0	0	40.0	50.0
2	15.1	2.92	20.0	42.1
3	12.2	6.72	40.0	35.4
4	12.2	13.4	40.0	26.9
5	9.5	13.1	40.0	34.4
6	16.1	30.0	40.0	26.7
7	17.5	52.8	40.0	25.7
8	17.5	118.5	48.0	28.5

a. Measured at 25°C.
b. Calculated as if the nitrogen dioxide were completely dissociated.

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It is clear that these results add further confirmation that nitrogen dioxide does inhibit the reaction at 181ºC. Expt. 1 where no nitrogen dioxide was added may be compared to expts. 2-8 where varying amounts were added.

The inhibition of the reaction by nitrogen dioxide has been explained by Phillips (e) as being due to a reversal of the first step and this explanation is incorporated into the mechanism written earlier. In the rate expression (7) it may be seen that the rate depends not only on the nitrogen dioxide, which lowers it, but on the nitric oxide which, according to this scheme, would raise it. In order to examine the inhibiting effect of nitrogen dioxide in detail it would be necessary to know both the nitrogen dioxide and the nitric oxide at all times. This was not done for the experiments of Table 2 and for this reason it seems worthwhile only to point out the qualitative features. It is for example clear that increasing amounts of nitrogen dioxide, expts. 2-8 do lower the rate more and more although after substantial amounts have been added further addition seems to have no effect, expts. 5-8. The accelerating effect of large amounts of nitrogen dioxide reported by Pollard Wyatt and Marshall (j) has been noted at 161ºC in a previous report (f) but was not encountered at 181ºC as Table 2 shows. This point was not investigated further.

Oxygen. In a previous report (g) it has been noted that oxygen inhibits the thermal decomposition of n-propyl nitrate strongly. Table 3 shows that the same is true for ethyl nitrate.

Table 3

The Effect of Oxygen on the Rate of Decomposition

of Ethyl Nitrate at 181ºC

Initial Pressure
(mm)

Exp.	Ethyl Nitrate	Oxygen	t (min.)	Percent Reaction
1	---[a]	0	20.0	28
2	19.5	55.5	20.0	8.9
3	20.9	57.1	40.0	38.3
4	---[a]	0	85.0	83.3
5	19.5	52.0	85.0	46.2

- - - -

[a] value interpolated from reaction rate data (f)

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Oxygen can inhibit the decomposition by removal of the nitric oxide from the scene as soon as it is formed.

$$2NO + O_2 \longrightarrow 2NO_2$$

At 181°C this equilibrium would be completely to the right. In effect this lowers the rate of step (2) and allows the reverse of step (1) to compete with it more effectively resulting in a lower rate*.

Nitric Oxide. The effect of nitric oxide on the thermal decomposition of ethyl nitrate has not yet been explored. In a previous report from this laboratory (g) it was noted that nitric oxide altered the product composition but had little effect on the rate for the case of n-propyl nitrate.

In terms of the reaction scheme described earlier a study of the effect of nitric oxide should be a good test for the ideas discussed here. The results of a series of experiments are shown in Table 4 and fig. 1.

Table 4

The Effect of Nitric Oxide on the Rate
of Decomposition of Ethyl Nitrate at 181°C

Expt.	Initial Pressure (mm)		t (min.)	Percent Reaction	k^b $(mm.^{-1})$
	Ethyl Nitrate	Nitric Oxide			
1	---a	0	20.0	28.0	
2	19.9	3.2	20.0	32.2	
3	22.0	16.6	20.0	55.9	0.0405

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* At the symposium "The Chemistry of the Oxides of Nitrogen" sponsored by the Office of Ordnance Research at Chicago, Sept. 3 and 4, 1953, Professor Richard A. Ogg, Jr. of Stanford University, reported the reaction

$$2C_2H_5ONO + NO_2 + O_2 \longrightarrow 2C_2H_5ONO_2 + NO_2.$$
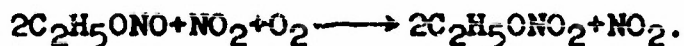
as occurring at room temperature via the species NO_4. If this reaction is also important at the temperatures involved here it would constitute another route for the inhibition by oxygen.

The question arises as to whether this reaction could also serve as an explanation for the inhibiting effect of nitrogen dioxide itself. Such an explanation would require ethyl nitrite to inhibit the reaction too. Since it has been shown (f) that ethyl nitrite does not affect the reaction rate it may be concluded that the inhibiting effect of nitrogen dioxide is best explained by its reaction with the ethoxyl radical as discussed earlier.

Table 4 (Cont'd.)

The Effect of Nitric Oxide on the Rate

of Decomposition of Ethyl Nitrate at 181°C

Expt.	Initial Pressure (mm)		t (min.)	Percent Reaction	k^b (mm.$^{-1}$)
	Ethyl Nitrate	Nitric Oxide			
4	21.2	35.0	20.0	65.5	0.0530
5	21.2	60.0	20.0	69.0	0.0583
6	18.5	41.8	12.0	50.7	0.0592
7	19.5	37.4	80.0	94.4	0.036

- - - -

[a] Interpolated from rate date (b).

[b] First order constant.

In carrying out these experiments it could be observed visually
that much more nitrogen dioxide was being formed than in those
carried out with ethyl nitrate alone. That this is so is clearly
shown in Fig. 1 where the production of nitrogen dioxide and
ethyl nitrite are plotted vs. percent reaction. For comparison
the results for the production of nitrogen dioxide for the de-
composition of ethyl nitrate alone are included. The addition
of nitric oxide increases the maximum yield of nitrogen dioxide
by about four fold. The production of ethyl nitrite as shown in
Fig. 1 also rises to a greater height corresponding to about 80%
of the ethyl nitrate decomposed. It may be noted here that since
nitric oxide boosted the rate, less time was required to get
essentially complete reaction so that for example for 50%
reaction only about 12 minutes was required (vs. about 40 for
ethyl nitrate alone). Thus the ethyl nitrite had less time to
decompose and this helped to keep its yield high.

The results shown in Fig. 1 are readily explained on the basis
of the reaction picture discussed earlier. In the presence of
excess nitric oxide the effective result of the thermal decom-
position of ethyl nitrate would be

$$C_2H_5ONO_2 + NO \longrightarrow C_2H_5ONO + NO_2$$
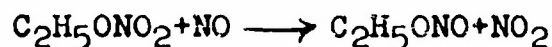
If the yields of ethyl nitrite and of nitrogen dioxide are
plotted against percent reaction the result should be a straight
line of unit slope. Such a line is drawn in Fig. 1. It is

seen that the ethyl nitrite points fall on this line fairly
well until near the end of the reaction where the last ethyl
nitrite point is below the line. In the earlier part of the
reaction the nitrogen dioxide points also are near the line
but fall away from it in the later stages. The tendency of
the ethyl nitrite and nitrogen dioxide points to fall away
from the line in the later part of the reaction is attributable
to the intervention of the thermal decomposition of the ethyl
nitrite itself. Since the decomposition of one ethyl nitrite
molecule would give products that would reduce several nitro-
gen dioxide molecules it is understandable that the dropping
off of the nitrogen dioxide points should be the more pro-
nounced of the two.

The kinetic results of Table 4 also are consistent with this.
The addition of nitric oxide clearly increases the reaction
rate, expts. 1-5. The rate does not increase directly with
the amount of nitric oxide however. Experiments 2-5 are
comparable since they are for the same reaction time. The
increase in the percent reaction becomes smaller and smaller
as more nitric oxide is added. Thus the increase from 35 mm.
to 60 mm. of nitric oxide added in expts. 4 and 5 results in
only a 3.5% increase in the percent reaction. The last column
indicates that the reaction rate is approaching a limiting
value of about 0.06 min.$^{-1}$. This behavior is readily interpreted
in terms of rate equation (7). The addition of sufficient nitric
oxide makes the fraction in the denominator small compared to
one and the rate approaches the limiting value of k_1 which must
then be about 0.06 min.$^{-1}$. The kinetics in the presence of
nitric oxide are complicated by the fact that as the reaction
proceeds the production of nitrogen dioxide acts to lower
the rate. Experiment 7, for example, which is a long time run,
gives a rate constant lower than would have been found for a
shorter time under the same conditions of nitric oxide addition.
It may be emphasized again that since addition of very large
amounts of nitric oxide, cf. expt. 4 and 5, do not cause a
corresponding increase in the rate the reaction cannot involve
direct attack on nitric oxide on the ethyl nitrate molecule.
The above features do however fit in very well with the
assignment to nitric oxide of its role in pulling the equilibrium
of step (1) to the right.

Acetaldehyde. The results of some experiments with acetalde-
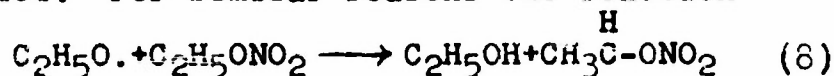hyde are shown in Table 5.

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Table 5

The Effect of Acetaldehyde on the Rate

of Decomposition of Ethyl Nitrate at

$181^{\circ}C$

Expt.	Ethyl Nitrate	Initial Pressure (mm.) Acetaldehyde	t (min.)	Percent Reaction	k (mm.$^{-1}$)
1	26.4	0	25.0	30.4	
2	22.0	0	40.0	50.0	
3	20.0	10.0	10.0	32.0	0.038
4	19.5	20.0	10.0	43.6	0.057
5	20.0	30.0	10.0	45.0	0.060
6	18.5	16.7	20.0	65.0	0.052
7	19.5	20.0	40.0	85.9	0.049

Comparison of the results of expts. 3-7 where acetaldehyde was added to expts. 1 and 2 where none was added show that it acts to accelerate the reaction. It is well known (k) that acetaldehyde and nitrogen dioxide react rapidly at $181^{\circ}C$ to remove the nitrogen dioxide, and to furnish nitric oxide. In accordance with this only traces of nitrogen dioxide could be observed in expts. 3-7. If the acetaldehyde were able to keep the nitrogen dioxide concentration very low the observed rate, as in the case of nitric oxide should approach k_1 as a limit. The rate constants observed in expts. 4 and 5 are in fair agreement with those found for the limiting rates with nitric oxide.

Diethyl Peroxide: Diethyl peroxide has been used as a source of ethoxyl radicals in a study of the ethyl nitrite decomposition (1). The weight of the evidence for that reaction was that ethoxyl and ethyl nitrite did not react in the temperature range ($\sim 181^{\circ}C$) studied. For similar reasons the reaction

$$C_2H_5O. + C_2H_5ONO_2 \longrightarrow C_2H_5OH + CH_3\overset{H}{\underset{.}{C}}-ONO_2 \qquad (8)$$

is not considered to be of importance for the ethyl nitrate decomposition. A few experiments have been carried out wherein diethyl peroxide was added to ethyl nitrate. The results are shown in Table 6.

Table 6

The Effect of Diethyl Peroxide on the

Thermal Decomposition of Ethyl Nitrate

at 181°C

Expt.	Initial Pressure (mm.)		t (min.)	Percent Reaction	k (mm.$^{-1}$)
	Ethyl Nitrate	Diethyl Peroxide			
1	18.9	11.2	10	45	0.059
2	20.2	23.0	10	39	0.041
3	18.9	11.2	20.1	56	0.046
4	20.2	23.0	20.1	60	0.048

The main point of the above experiments was that sufficient ethoxyl radicals were generated from the diethyl peroxide to bring about complete decomposition of ethyl nitrate via (8). In no case did this occur. The rate constants found are intermediate between these for the reaction of ethyl nitrate alone and the limiting rate obtained with nitric oxide and acetaldehyde. The ethoxyl radicals produced by diethyl peroxide would be able to bring about reduction of the nitrogen dioxide to nitric oxide either via steps (3) - (5) of the mechanism written earlier or via the formation of its own end products, acetaldehyde and formaldehyde.

An alternative explanation for the results of Table 6 might be argued. If (8) were truly a fast reaction, the rapid decomposition of the

$$CH_3\overset{H}{\underset{.}{C}}-ONO_2$$
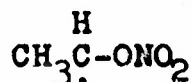
radical to give nitrogen dioxide followed by the combination of the nitrogen dioxide with ethoxyl radical to regenerate ethyl nitrate would mask the existence of (8). This would result in the formation of large amounts of acetaldehyde. The absorption at the acetaldehyde carbonyl region was of the same small order of magnitude as in the decomposition of ethyl nitrate alone, however, and hence this explanation is ruled out.

The Importance of Nitromethane as a Reaction Product. It is clear that the results of the foregoing experiments with additives offer strong support for the picture of the reaction presented in

the Introduction. The discussion of these results is relevant chiefly to steps (1) and (2) of the mechanism. The observation of nitromethane and nitroethane as products of the thermal decompositions of ethyl and n-propyl nitrates respectively fits in well with steps (3) - (5). Although nitroethane was one of the major products found in the n-propyl nitrate case (g) nitromethane was a comparative minor product in the ethyl nitrate decomposition (f) and its presence was noted qualitatively without any attempts at a quantitative appraisal. The chief obstacle to the determination of the nitromethane using its infrared absorption at $6.3 - 6.4\mu$ is the interference of the adjacent ethyl nitrite band. Since the ethyl nitrite is a good deal more volatile than nitromethane it was possible to effect a separation of these two compounds using a system of cold traps and thus to get quantitative data on the formation of nitromethane in the thermal decomposition of ethyl nitrate. This has been done at $181^{\circ}C$ and the results are shown in Table 7.

Table 7

Nitromethane Yield at $181^{\circ}C$

Expt.	Initial Pressure of Ethyl Nitrate (mm.)	Percent Reaction	Yield of Nitromethane Based on Ethyl Nitrate Reacted
1	17.3	37.5	8.6 %
2	17.3	80	8
3	23	79	8.1
4	30.0	100	9

Thus at $181^{\circ}C$ nitromethane represents 8 - 9% of the reaction product.

The Mechanism of the Reaction: In an earlier report (i) the reduction of nitrogen dioxide by formaldehyde has been considered as a possible source for the nitric oxide required. The stoichiometry of this reaction has been reported as (1)

$$5CH_2O+7NO_2 \longrightarrow 3CO+2CO_2+7NO+5H_2O \qquad (9)$$

If the amounts of nitromethane indicated in Table 6 measure the amounts of formaldehyde present it is clear that (9) could not possibly account for the high yields of ethyl nitrite, 70 - 75%, obtained in the thermal decomposition of ethyl nitrate by itself (f). It is thus clear that some species in the reaction mixture
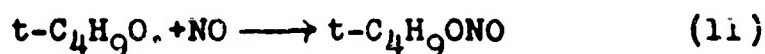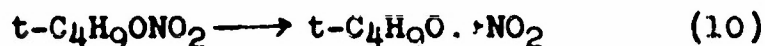
must be reacting rapidly with nitrogen dioxide to yield nitric oxide and that, in view of the high ethyl nitrite yield, one molecule of the species must reduce several nitrogen dioxide molecules.

Examination of the system suggests two possible species that might perform this function, viz. ethoxyl radical or methyl radical. Of these it is possible to present evidence that the methyl radical undergoes a reaction of the type

$$NO_2 + CH_3. \longrightarrow NO + \text{oxidation products.}$$
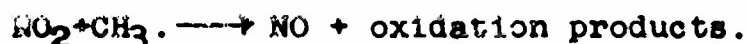
This evidence arises from two sources.

Evidence for the Nitrogen Dioxide-Methyl Radical Reaction from the T-Butyl Nitrate Studies. One piece of evidence for the nitrogen dioxide-methyl reaction arises from the study of the thermal decomposition of t-butyl nitrate. It has been found (g) that t-butyl nitrite is a major product of this reaction. According to the present shceme this must arise as follows:

$$t-C_4H_9ONO_2 \longrightarrow t-C_4H_9O. + NO_2 \qquad (10)$$

$$t-C_4H_9O. + NO \longrightarrow t-C_4H_9ONO \qquad (11)$$

The nitric oxide can be formed only by the reduction of the nitrogen dioxide. This in turn can be reduced most plausibly either by acetone or the methyl radical.

$$t-C_4H_9O. \longrightarrow CH_3. + (CH_3)_2CO \qquad (12)$$
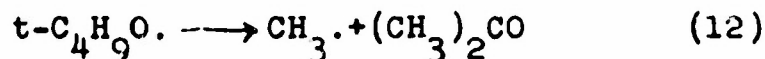
It was possible to show that acetone does not reduce nitrogen dioxide at this temperature (181°C). Thus when 40 mm. of acetone and 8.8 mm. of nitrogen dioxide were heated together at 181°C for 60 minutes no reaction occurred and the starting materials were recovered unchanged. This leaves only the methyl radical as a plausible reactant.

Evidence from the Nitrogen Dioxide-Acetaldehyde Reaction. The above evidence is supplemented by the results obtained by Dr. Luther Browning of the Bureau of Mines in a study of the nitrogen dioxide-acetaldehyde reaction *. Dr. Browning's results bear directly on some of the ideas expressed here and will be discussed in some detail.
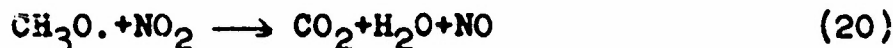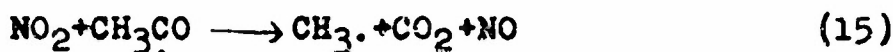
Nitrogen dioxide and acetaldehyde react readily in the temperature range 100 - 140°C. Previous workers (k) have suggested
- - - -

* The author wishes to thank Dr. Browning for making the results of his work available.

that the reaction may be expressed

$$NO_2 + CH_3CHO \longrightarrow CH_3COOH + NO \qquad (13)$$
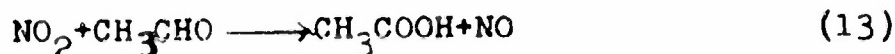
Dr. Browning has shown that the reaction is not so simple
however. The main products of the reaction at the temperatures
mentioned are actually nitric oxide, nitromethane and methyl
nitrate with methyl nitrite appearing in the later stages.
Dr. Browning explains these results on the following basis:

$$CH_3CHO + NO_2 \longrightarrow CH_3\overset{.}{C}O + HONO \qquad (14)$$

$$NO_2 + CH_3\overset{.}{C}O \longrightarrow CH_3. + CO_2 + NO \qquad (15)$$

$$CH_3. + NO_2 \longrightarrow CH_3NO_2 \qquad (16)$$

$$CH_3. + NO_2 \longrightarrow CH_3O. + NO \qquad (17)$$

$$CH_3O. + NO \longrightarrow CH_3ONO \qquad (18)$$

$$CH_3O. + NO_2 \longrightarrow CH_3ONO_2 \qquad (19)$$

$$CH_3O. + NO_2 \longrightarrow CO_2 + H_2O + NO \qquad (20)$$

The fact that methyl nitrite is found only in the later stages
of the reaction when nitric oxide is present in abundance
rules out the reaction

$$CH_3. + NO_2 \longrightarrow CH_3ONO \qquad (21)$$

as the source for the methyl nitrite. Thus the interesting
fact emerges that methyl radical reacts directly with nitrogen
dioxide to give nitromethane but not to give methyl nitrite.
A plausible explanation may be made for this. The formation
of the C-O bond in (21) results in a molecule having an excess
energy equal to the C-O bond energy - about 77.5 kcal./mole (m).
For the molecule to stabilize itself this energy must be re-
distributed in the molecule or lost by collision. The N-O bond
in that molecule however requires only about 40 ckal. for its
rupture so that about 38 kcal. per mole would have to be dissi-
pated. The result is that each time the methyl nitrite molecule
formed via (21) it would immediately rupture at the O-N bond
and the net result would be that of (17). In the case of
reaction (16) the excess energy is the C-N bond energy - about
52 kcal. (n). Here there is no weaker bond than that being
formed and a loss or redistribution of only a little of the
energy will stabilize the molecule.

The above picture does require that nitrogen dioxide and
methyl radicals react in an oxidation reduction reaction
and thus supports the mechanism for the nitrate ester de-
composition. These arguments do not rule out a direct
reaction between ethoxyl and nitrogen dioxide to give nitric
oxide but since the case for methyl radical is so plausible
discussion will be based on it.

The Question of Methyl Nitrate Formation in the
Thermal Decomposition of Ethyl Nitrate. The nitrogen
dioxide-acetaldehyde results suggest that methyl nitrate
should be formed in the thermal decomposition of ethyl
nitrate too via step (18). In an earlier report from this
laboratory nitromethane and methyl nitrite have been re-
ported as products (f) but methyl nitrate has not. The
basis for the analytical method was laid down in the same
report and an effort was made to demonstrate that the
infrared absorptions used for the analyses measured the
compounds that they were assigned to. The spectrum for
ethyl nitrate is shown in fig. 2 and that for methyl nitrate
in fig. 3. They are very similar both having strong absorp-
tions in the regions of 6 μ, 7.75 μ and 11.75 μ and weaker
absorptions in the regions of 3.4 μ, 7 μ and 9.75 μ. The
main differences are that methyl nitrate has no absorption
at 11.0 μ where ethyl nitrate has a weak one and that the
ethyl nitrate absorption at 7 μ is relatively weaker than
that of methyl nitrate.

One test that was applied to the analytical method was to
compare the spectra of synthetic mixtures made up to dupli-
cate the decomposition mixtures with the spectra of the
decomposition mixtures themselves. Figs. 4, 5, and 6 are
reproduced from the earlier report for mixtures correspond-
ing to from 33.4 to 61.5% decomposition. Due to the cell
face absorption in the 7 μ region it seems best to examine
the 11 μ region. Here the presence of appreciable methyl
nitrate in the decomposition mixtures should result in the
synthetic mixture spectrum showing a more intense absorption
at 11 μ even if there was agreement at the 11.73 μ peak.

Examination of Fig. 4 for 33.4% decomposition shows exact
agreement for both peaks. The 44.0% and 61.5% decomposition
mixtures indicate the possible presence of small amounts of
methyl nitrate for here the synthetic mixtures do absorb more
strongly in the 11 μ region. The situation is not quite as
simple as this unfortunately. Ethyl nitrite (f) has an
absorption at 10.75 μ. At the higher percent reaction a com-
paratively large amount of ethyl nitrite is present and the ethyl
nitrite absorption makes a strong contribution to the absorption
in the 11 μ region. This tends to make any contribution attributable

to methyl nitrate a small difference between large quantities and hence not very reliable. This is not the case for Figs. 4 and 5 where the percent reaction is smaller and the ethyl nitrate is present in substantially greater amount than the ethyl nitrite. It seems fairly safe to say that very little methyl nitrate can be present in at least the first 50% of the reaction. It is pertinent to this that methyl nitrate apparently decomposes more slowly than ethyl nitrate (b). (Some preliminary experiments in this laboratory indicate a value of $k = 0.005$ mm.$^{-1}$ at 181°C. as compared to $k = 0.02$ mm.$^{-1}$ for ethyl nitrate at the same temperature.) Thus any methyl nitrate formed would accumulate in the reaction and be most evident in the later stages.

A fairly plausible explanation can be given as to why methyl nitrate was found in substantial amount in Dr. Browning's study of the nitrogen dioxide-acetaldehyde reaction but is formed in only very small amounts, if at all, in the ethyl nitrate decomposition. The ethyl nitrate work was carried on at 161 - 201°C. while the nitrogen dioxide-acetaldehyde reaction was studied at 100 - 140°C. The competing reactions which are of interest are

$$NO_2 + CH_3O. \longrightarrow CH_3ONO_2$$

$$NO_2 + CH_3O. \longrightarrow \text{oxidation}$$
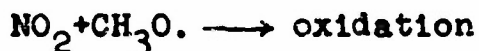
For the first, since the only thing happening is the formation of a bond, the activation energy may be expected to be very small if not zero. It is hard to say what the activation energy for the second reaction is but it is undoubtedly greater than zero. Thus the increase in temperature in going from the range 100 - 140°C. to 161 - 201°C. could easily result in the oxidation reaction becoming much more important than the bond formation reaction.

The entire reaction between nitrogen dioxide and methyl radicals represents only a minor fraction of the reaction path and if of this fraction only a minor fraction goes to methyl nitrate the absolute amount of methyl nitrate could easily be small enough to escape detection.

The exact products of the oxidation of methyl radicals by nitrogen dioxide have not been determined. The reaction of these two species is undoubtedly complex but the stoichiometry could be written

$$7NO_2 + 2CH_3 \longrightarrow 2CO_2 + 3H_2O + 7NO$$
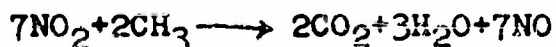
If this is incorporated into the reaction scheme, the overall reaction for the thermal decomposition of ethyl nitrate may be written

$$12C_2H_5ONO_2 \longrightarrow 9C_2H_5ONO + 4CO_2 + 2NO + 5H_2O + CH_3NO_2 + CH_2O$$
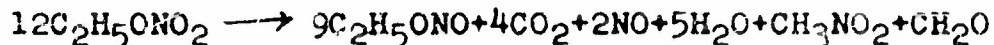
This is not intended as an accurate description of the stoichiometry but it does show that the postulated oxidation of methyl radicals yields sufficient nitric oxide to give the observed reaction products in their proper amount.

The Kinetics of the Reaction. In previous studies of the thermal decomposition of ethyl nitrate (c, e. f) it has been found that when the data have been plotted as if the reaction were first order the curves obtained have not been simple straight lines. In general a fairly linear initial section has been followed by an apparently fairly linear later section of higher slope. It has been demonstrated in an earlier report (f) that the general rate expression found using the initial slopes for reaction rates agrees well with that reported by Bawn and Adams (c) while the expression found from the later slopes agrees well with the expression reported by Phillips (e). The foregoing discussion indicates that it is not correct to equate such activation data with any particular reaction such as the initial N-O bond cleavage. The reaction is so complicated that a clear interpretation of these kinetic curves does not seem possible.

The results of the addition of nitric oxide and acetaldehyde suggest another approach -- to wit the simplification of the reaction conditions. According to the picture developed in this discussion the addition of nitric oxide and acetaldehyde tends to eliminate the reverse of step (1). If this reverse step could be completely eliminated then the rate of disappearance of ethyl nitrate would measure directly the rate of the initial N-O bond cleavage. This has been accomplished by carrying out the decomposition of ethyl nitrate in the presence of nitric oxide and acetaldehyde together. The nitric oxide serves to react with the ethoxyl radical while the acetaldehyde serves to destroy the nitrogen dioxide as it is formed. The reaction was studied in this way at $161^\circ C.$, $171^\circ C.$, and $181^\circ C.$ and the rate data appear in Figs. 7, 8, and 9. The experimental data for $181^\circ C.$ are shown in Table 8 and are typical.

Table 8

The Thermal Decomposition of Ethyl Nitrate in the

Presence of Nitric Oxide and Acetaldehyde at 181°C

Expt.	Initial Pressure (mm.)			t (min.)	% Reaction
	Ethyl Nitrate	Nitric Oxide	Acetaldehyde		
1	20.2	20.0	20.0	2.0	1.5
2	20.5	20.0	20.0	4.0	12.8
3	20.0	23.0	23.0	6.0	21.5
4	20.0	23.0	23.0	12.0	50.0
5	20.0	33.0	25.0^a	15.0	57.2
6	21.0	20.0	20.0	20.0	67.4
7	21.0	20.0	20.0	30.0	82.1
8	20.5	20.0	20.0	40.0	88.7
9	20.0	33.0	30.0^a	46.8	92.4

^{a}Here formaldehyde was used instead of acetaldehyde.

Here too it was desirable to show that the formation of methyl nitrate from the nitrogen dioxide-acetaldehyde reaction did not introduce any errors. This was done by carrying out checking experiments at 161°C and 181°C wherein formaldehyde was used in place of acetaldehyde. The results are shown in Figs. 7 and 9 and it can be seen that the points for formaldehyde fall on the curves within experimental error.

The rates calculated from the above data are given in Table 9.

Table 9

The Thermal Decomposition of Ethyl Nitrate in

the Presence of Nitric Oxide and Acetaldehyde

	161°C	171°C	181°C
Rate Constant (min.$^{-1}$)	0.00752 ± 0.00002	0.0218 ± 0.0002	0.0611 ± 0.0009

The general rate expression calculated from these data is

$$k = 10^{16.85} \, e^{\frac{-41,230 \pm 495}{RT}} \text{ sec.}^{-1}$$

This expression is calculated from the two extreme values and the error in the activation energy is calculated from the errors in these two rate constants. The precision of the data may be shown by the calculation of the 171°C rate using the above expression. The rate calculated is $k = 0.0221$ min.$^{-1}$ in excellent agreement with the measured rate.

It may be noted that activation energy found here is higher than the values reported by others which ranged from about 36 kcal.[c] to 39.9 kcal.[e]. Because of the techniques employed here it is felt that the value 41,290 kcal. is the correct value for this reaction and that it may with justification be equated to the N-O bond energy. The value for this bond energy has generally been taken as 34-37 kcal. per mole on the basis of studies on the nitrite esters. However the nitrite ester studies have met with some criticism (see ref. (n)) and it is possible that a reexamination of their decomposition may result in a higher activation energy. Such a study is going on in the laboratory and will be reported in the near future.

The frequency factor found here $10^{16.85}$ sec^{-1} is high for a a first order reaction. The value usually found is $10^{13} - 10^{14}$ sec^{-1}. In terms of the transition state theory of reaction rates this means that the entropy of activation has a significant positive value rather than being close to zero as is the usual case. The above value of the frequency factor, $10^{16.85}$ sec^{-1}, requires a value for ΔS activation of about 15 cal. per mole. High frequency factors have often been found for the thermal decomposition of nitrate esters, especially polynitrates (e). There is no obvious reason why such a high entropy of activation should be found for a simple alkyl nitrate but without an intimate knowledge of the relative structures of the ethyl nitrate molecule and its transition state there is little profit in speculating on this point.

SUMMARY

The effect of the addition of nitrogen dioxide, nitric oxide, acetaldehyde, oxygen and diethyl peroxide on the thermal decomposition of ethyl nitrate at 181°C have been studied. It has been found that nitrogen dioxide and oxygen inhibit the reaction and that nitric oxide, acetaldehyde and diethyl peroxide accelerate it.

The results of these studies give strong support to a mechanism for the thermal decomposition of nitrate esters which was proposed in preliminary form in an earlier report and which was completed in this one.

On the basis of the mechanism proposed it was possible to carry our the thermal decomposition of ethyl nitrate in such a way that the kinetics were truly first order and where the activation energy could be properly interpreted in terms of the N-O bond energy. The rate expression so found was

$$k = 10^{16.85} e^{\frac{-41,290}{RT}} \text{ sec.}^{-1}.$$

ACKNOWLEDGMENTS

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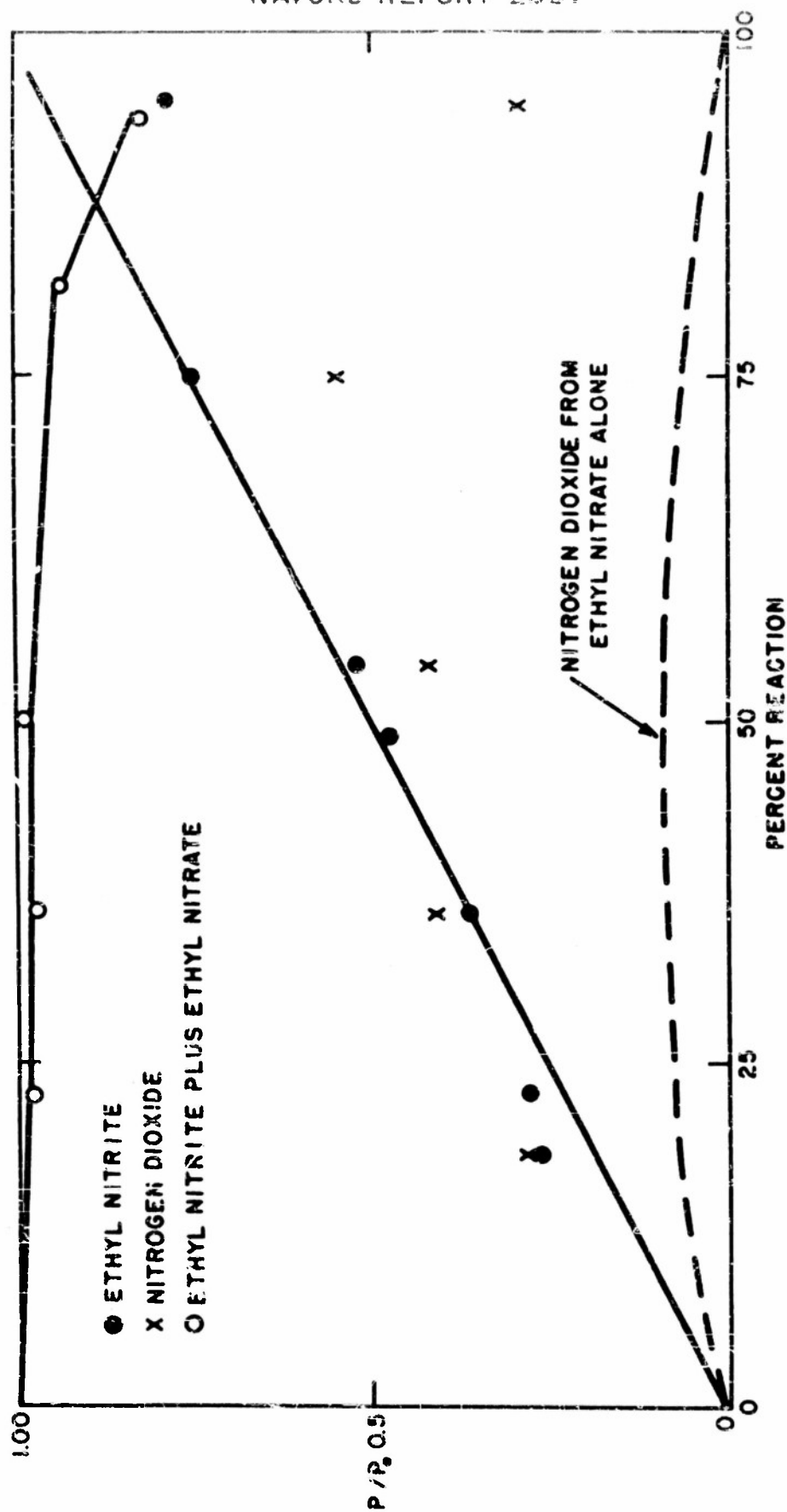
FIG. I PRODUCTS OF THE THERMAL DECOMPOSITION OF ETHYL NITRATE IN THE PRESENCE OF NITRITE OXIDE AT 181°C
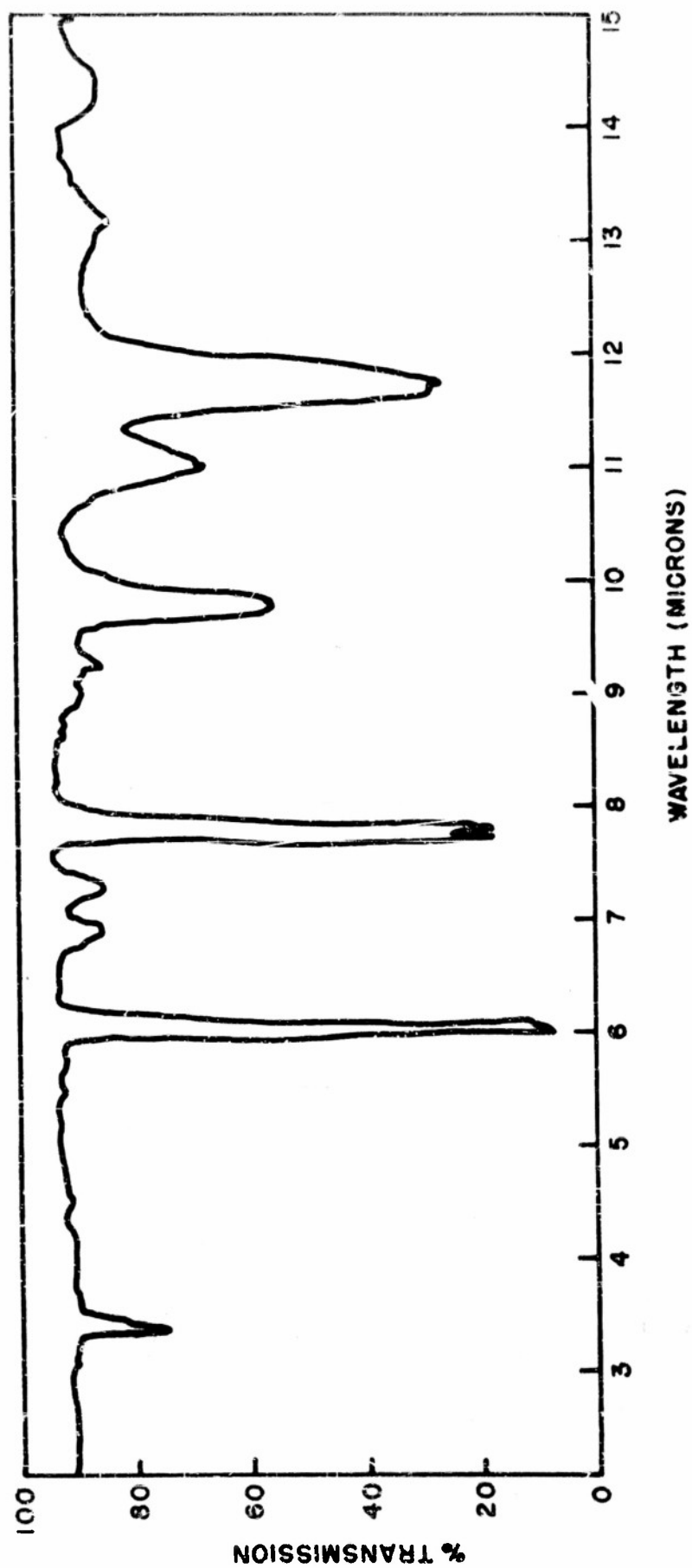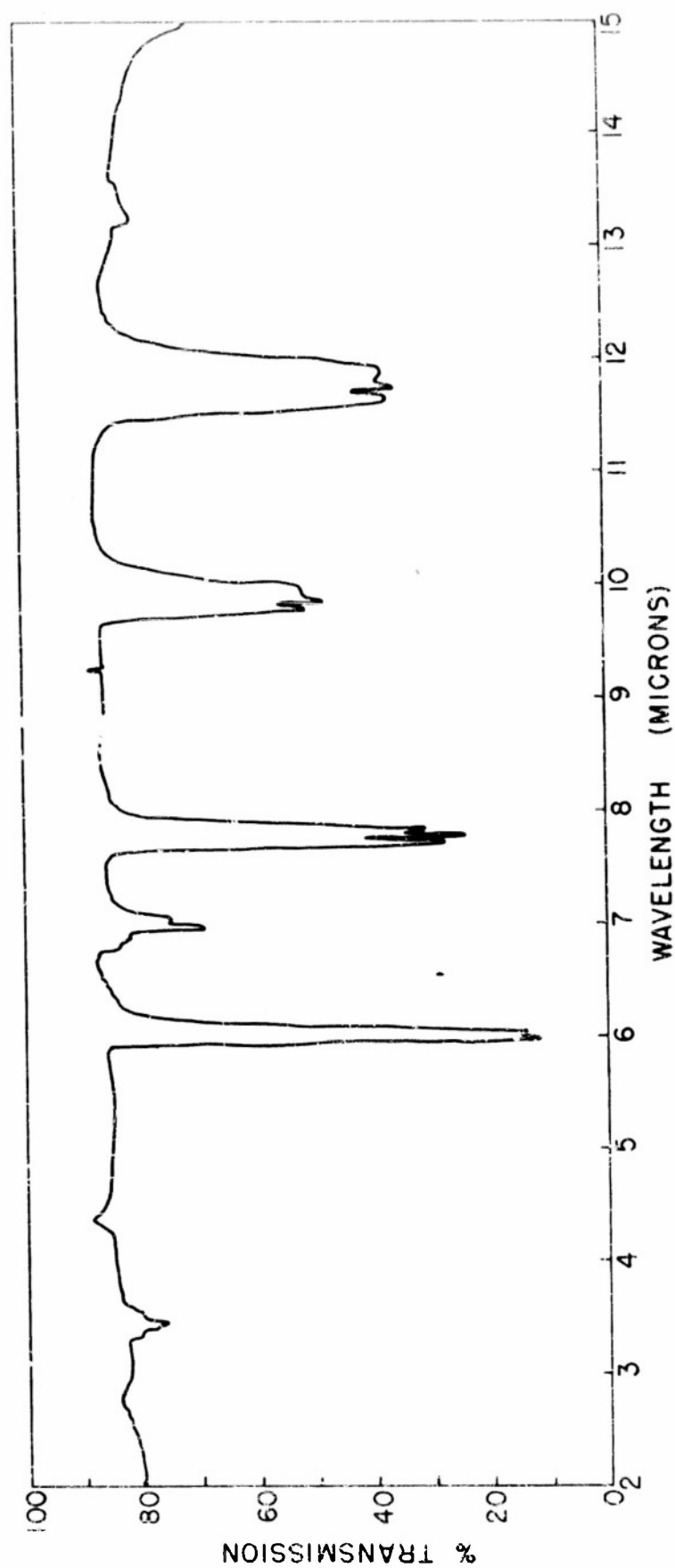
FIG. 2 ETHYL NITRATE P=19 MM L-52 MM

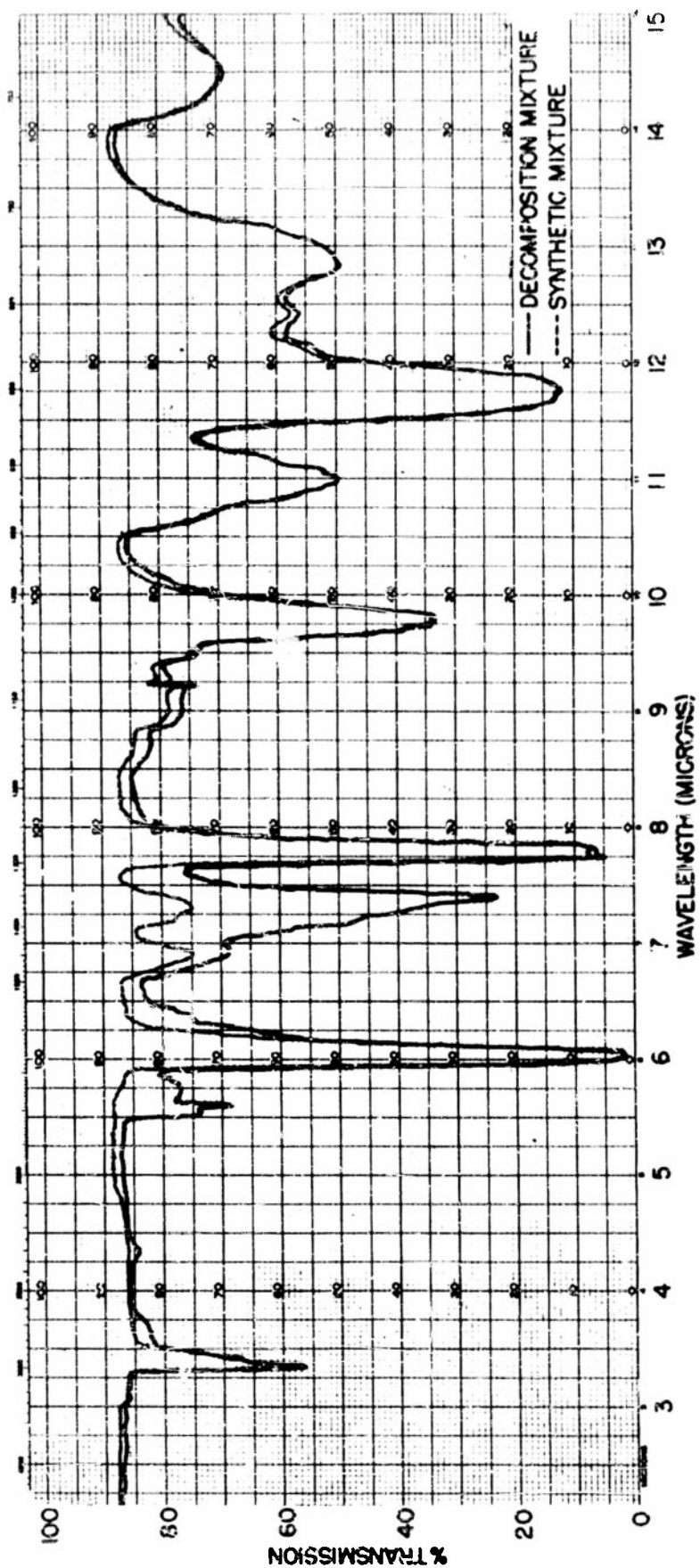FIG. 3 METHYL NITRATE P=10.5 MM CELL LENGTH=52.0 MM

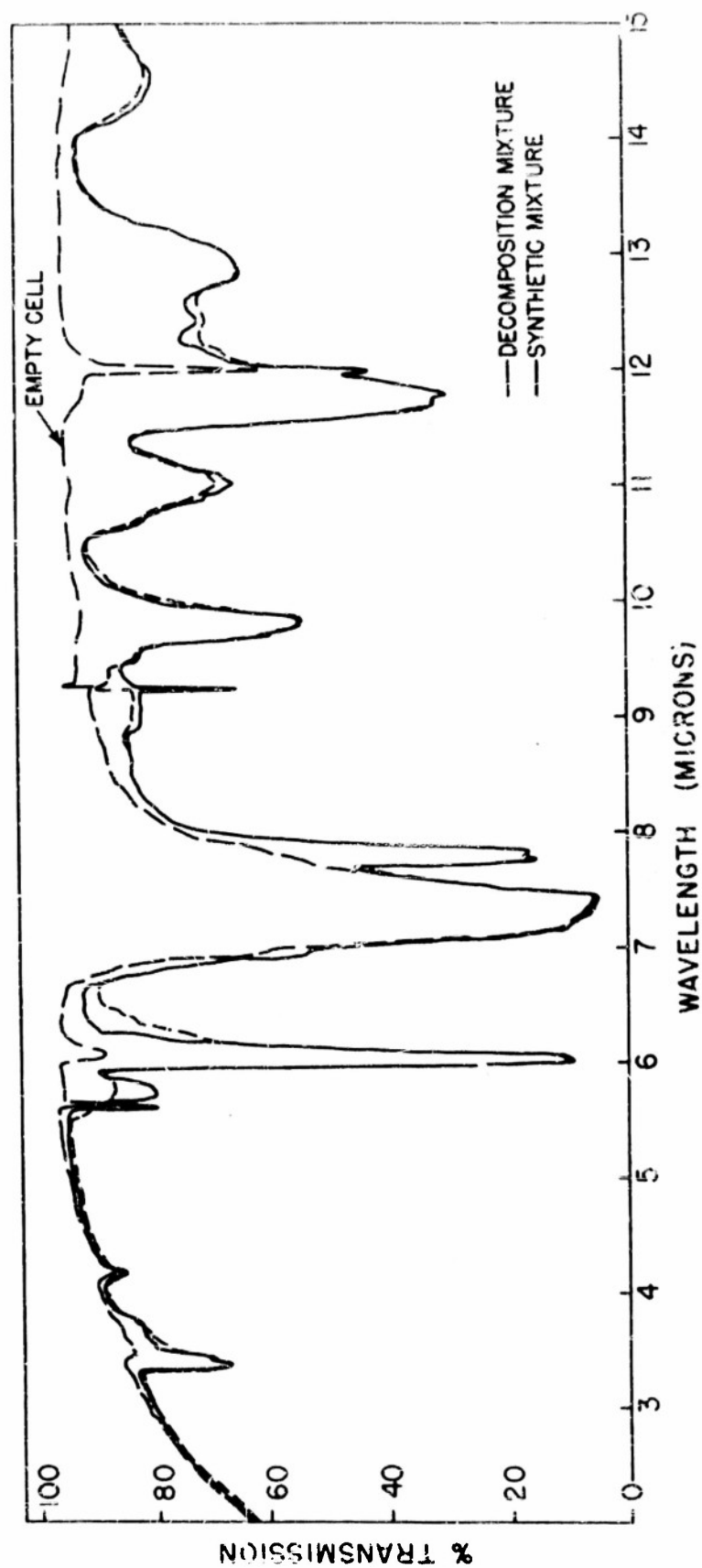FIG. 4 COMPARISON OF 33.4% DECOMPOSITION MIXTURE AND SYNTHETIC MIXTURE

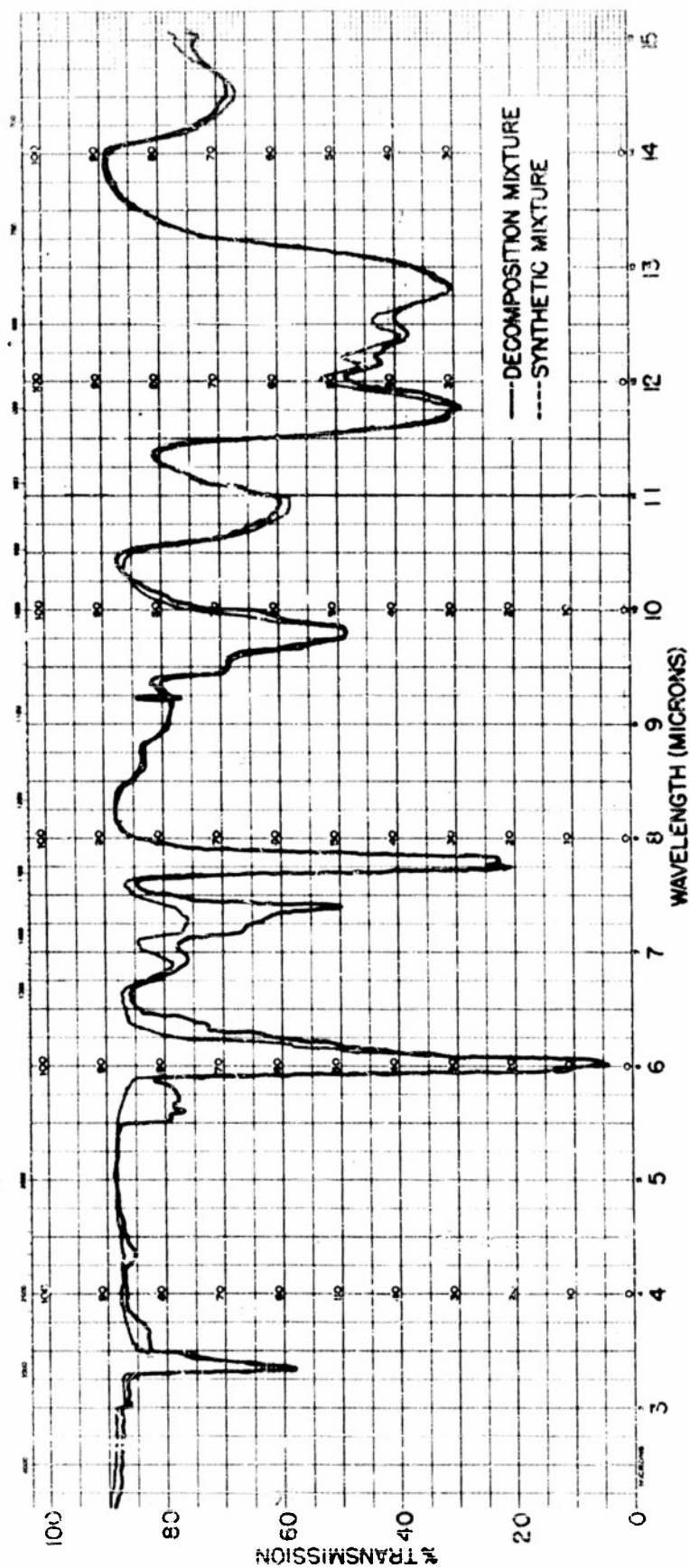FIG 5 COMPARISON OF 44.0% DECOMPOSITION MIXTURE AND SYNTHETIC MIXTURE

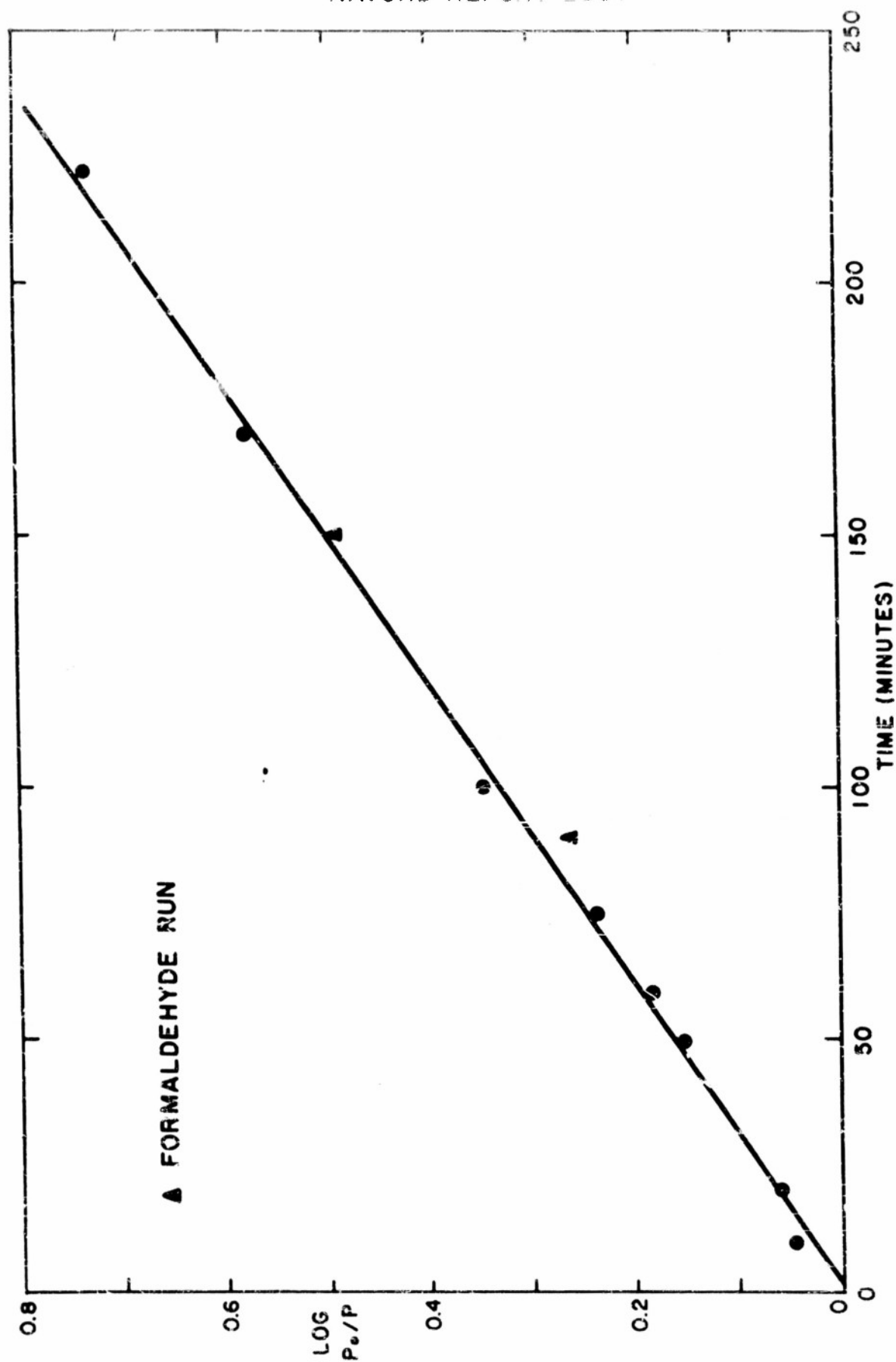FIG. 6 COMPARISON OF 61.5% DECOMPOSITION MIXTURE AND SYNTHETIC MIXTURE

FIG. 7 THE RATE OF DECOMPOSITION OF ETHYL NITRATE AT 161° C
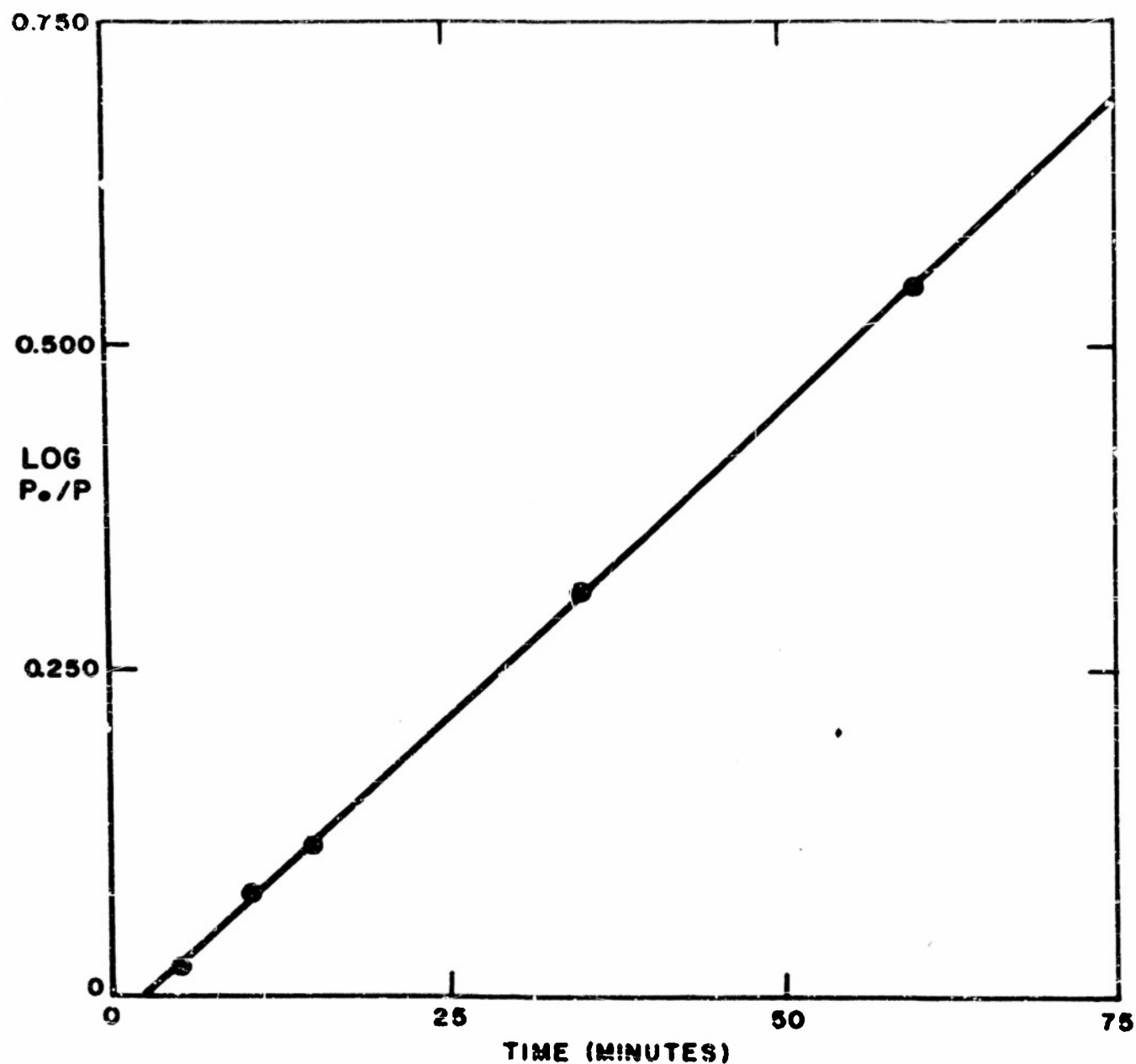IN THE PRESENCE OF NITRIC OXIDE AND ACETALDEHYDE

FIG. 8 THE RATE OF DECOMPOSITION OF ETHYL NITRATE
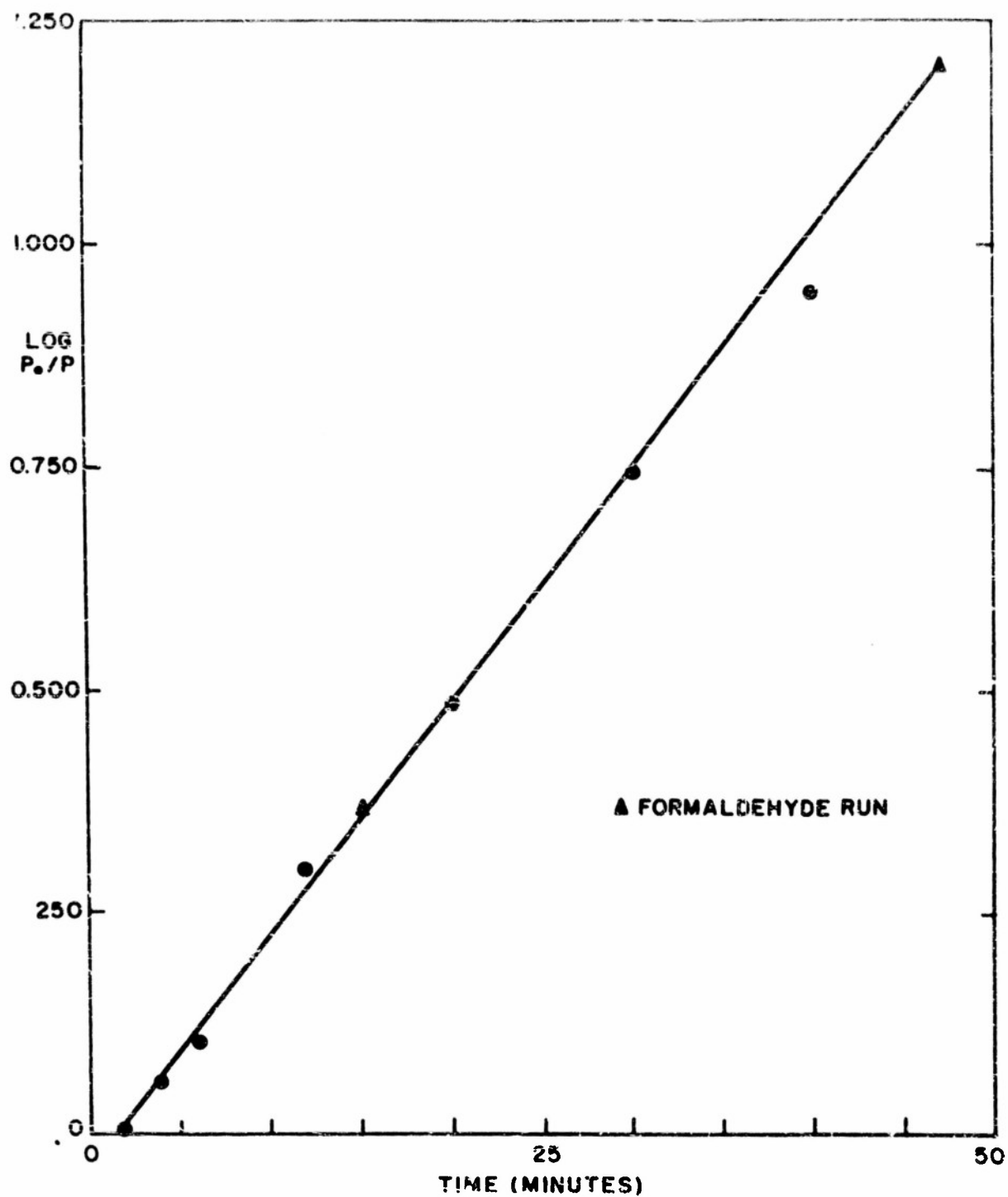AT 171°C PRESENCE OF NITRIC OXIDE AND ACETALDEHYDE

FIG. 9 THE RATE OF DECOMPOSITION OF ETHYL NITRATE AT 181°C
IN PRESENCE AT NITRIC OXIDE AND ACETALDEHYDE